

Wastewater treatment by adsorption with electrochemical regeneration using graphite-based adsorbents

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Abstract An innovative technology for wastewater treatment using adsorption and electrochemical regeneration has been developed at the University of Manchester. The process uses a low capacity graphitic adsorbent material (a graphite intercalation compound, NyexTM 1000) which can be regenerated electrochemically. In this study, we investigate the characteristics of a new, partially porous adsorbent material, NyexTM 2000 which offers increased surface area in comparison with NyexTM 1000. NyexTM 2000 was found to have an adsorption capacity of almost three times that of NyexTM 1000. The electrical conductivity of a NyexTM 2000 was found to be double that of NyexTM 1000, enabling improvements in the electrochemical regeneration characteristics. The removal of an anionic azo dye, acid violet 17, from aqueous solution using NyexTM 1000 and 2000 was investigated under various operating conditions. The adsorption of acid violet 17 on NyexTM 2000 was found to be comparatively fast with 75 % of the equilibrium capacity being achieved within 5 min. The parameters affecting the regeneration efficiency including the charge passed, current density, treatment time, adsorbent bed thickness, and pH were investigated. An electrochemical regeneration efficiency of around 100 % was achieved for a fully loaded NyexTM 2000 in a sequential batch electrochemical cell with a regeneration time of 60 min and a charge passed of 100 C g⁻¹ at a current density of 14 mA cm⁻². The charge required for electrochemical

regeneration was found to be approximately equal to theoretical charge required for complete oxidation of the adsorbed acid violet 17, making process design relatively simple. NyexTM 2000 was found to be an economic adsorbent with relatively small electrical energy consumption required (31 J mg⁻¹ of acid violet 17 treated, compared to 52 J mg⁻¹ of acid violet 17 for NyexTM 1000). Multiple adsorption/regeneration cycles presented no loss in adsorptive capacity and material losses over five adsorption/regeneration cycles.

Keywords Adsorption · Azo dye · Graphite intercalation compound · Electrochemical regeneration

1 Introduction

The pressure on industry to treat effluents effectively has increased due to public awareness regarding environmental and health effects caused by the industrial effluents and strict legislation enforced by environmental regulatory bodies. A wide range of industries such as textile, paper, plastic, food, leather and cosmetics use dyes or pigments to impart colour to their products. The presence of coloured organic compounds is aesthetically unacceptable to the public and can reduce light levels in water. A small concentration of organics can eliminate the aerobic activity within a water course [1]. The presence of some toxic organics can destroy aquatic life even in low concentrations [2]. Various chemical and physical techniques are being employed to meet the required standards of contaminants in industrial effluents, for example adsorption by activated carbon [3], flocculation and coagulation [4], sedimentation [5] and chemical oxidation [6]. However, the ultimate selection of a particular process mainly depends on the type of contamination and cost of the process.

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Adsorption has been widely used for the treatment of industrial effluents, and activated carbon is the most commonly used adsorbent material. However, once the adsorbent has been exhausted, it must be disposed of by land fill or incineration, or regenerated. Disposal of contaminated carbon can be costly and is environmentally undesirable. For large scale applications, thermal regeneration is normally used to recover the adsorbent. Thermal regeneration requires high energy and elevated cost along with 5–10 % material losses [7–9]. Regeneration accounts for about 75 % of the total operating and maintenance costs required for running an activated carbon adsorption process [10]. The high cost associated with the regeneration of activated carbon has led researchers to focus on the development of high capacity and low cost adsorbents for wastewater treatment applications. However, recovery and regeneration has remained a major issue for these adsorbents [11].

Various alternative regeneration methods have been investigated to try and reduce the regeneration cost. These processes include chemical or solvent regeneration [12], wet oxidative regeneration [13], microbial [14], ultrasonic [15] and electrochemical regeneration [8, 16–25]. Electrochemical regeneration by desorption or oxidation of organic adsorbate enables the restoration of the original capacity of the adsorbent. Studies of the electrochemical regeneration of granular activated carbon loaded with organics [16–20] have achieved regeneration efficiencies from 70 to 95 %. These studies have suggested that the best performance can be achieved with cathodic treatment, leading to desorption of the adsorbate [16, 20]. However, this method requires long regeneration times due to intra-particle diffusion within the porous activated carbon, high electrical energy consumption due to the relatively poor conductivity of activated carbon, and cathodic regeneration leads to a concentrated wastewater which will require further treatment.

Brown et al. [8, 21–23] have demonstrated the anodic electrochemical regeneration of a graphite-based adsorbent for the removal of phenol, crystal violet, atrazine and chlorinated hydrocarbons from aqueous solutions. The adsorbent material used, called NyexTM, was non-porous so that adsorption and electrochemical regeneration was rapid. NyexTM is a graphite intercalation compound (GIC) and is highly electrical conducting, so that the energy consumption during regeneration was found to be relatively small. Compared to activated carbon, the properties of the NyexTM adsorbent enabled rapid adsorption and electrochemical regeneration at the expense of reduced adsorption capacity, which was found to be around 1 mg g⁻¹ for phenol [23]. The process of adsorption with electrochemical regeneration using NyexTM is currently being commercialised by Arvia Technology Ltd., who have demonstrated

the process for a number of wastewater and waste treatment applications [24].

This study focuses on a recently developed adsorbent material which is a modified form of NyexTM 1000 (the adsorbent material currently used by Arvia Technology Ltd.) which aims to offer improved adsorption capacity for wastewater treatment applications while remaining suitable for electrochemical regeneration. An organic dye, acid violet 17, has been used as a model organic pollutant to determine the comparative performance of this new adsorbent (NyexTM 2000) and the existing adsorbent (NyexTM 1000). In addition to the study of adsorption characteristics of this material (in terms of the kinetics and isotherm) the electrochemical regeneration of this material has also been investigated.

2 Materials and methods

Acid violet 17 is an anionic azo dye used in the form of an aqueous solution prepared in the laboratory using deionised water, and previous studies of the adsorption and electrochemical regeneration of this dye have been reported [25]. The dye was provided by Kentex educational supplies under the trade name of Kenanthrol Violet 2B, which contains 22 % dye content with remainder inorganic fillers. The formula and molecular weight of acid violet 17 are C₄₁H₄₄N₃NaO₆S₂ and 761.92 g mol⁻¹, respectively. The concentration of dye in solution was determined using a Perkin-Elmer Lambda 10 spectrophotometer at a wavelength of 542 nm [25] after appropriate calibration.

2.1 Adsorbent materials

The adsorbent materials NyexTM 1000 and NyexTM 2000 were provided by Arvia Technology Ltd. NyexTM 1000 is a low cost GIC adsorbent while NyexTM 2000 was prepared by proprietary thermal and mechanical processing of NyexTM 1000 to increase its specific surface area. As previously reported [25], the particles of NyexTM 1000 are non-porous with a flake like structure and a particle size of order 500 µm. SEM images comparing the morphology of particles of NyexTM 1000 with NyexTM 2000 are shown in Fig. 1. Unlike NyexTM 1000, NyexTM 2000 has a rough surface morphology.

2.2 Adsorbent characterisation

The average particle size of the adsorbents was determined using a Malvern laser diffraction particle size analyser and the BET surface area, pore volume and pore diameter were determined using N₂ adsorption. Boehm surface titration [26] was carried out to determine the concentrations of the functional groups.

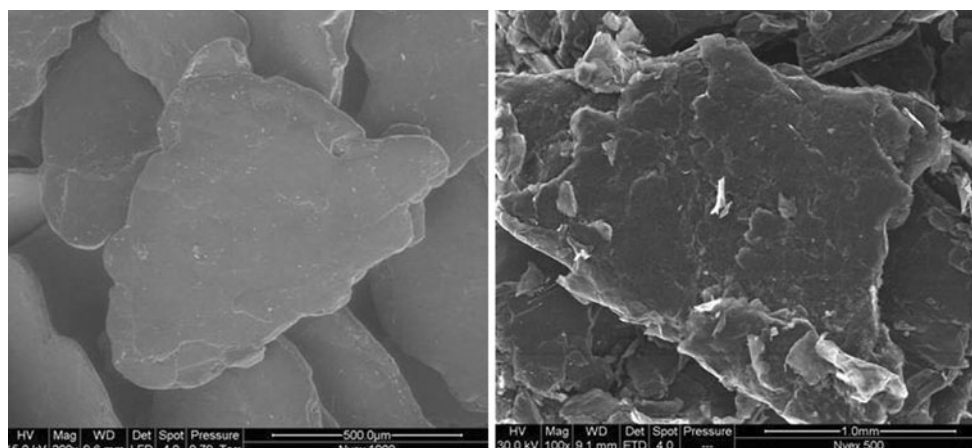


Fig. 1 SEM images of NyexTM 1000 (*left*) and NyexTM 2000 (*right*)

A sample of 5 g of each adsorbent was added to 100 mL of deionised water and the suspension was stirred for 24 h to achieve equilibrium. The final pH of the water, measured using a pH meter, was recorded as an indication of the adsorbent surface pH.

The surface charge (zeta potential) of the adsorbents was determined by electrophoretic mobility measurements carried out using a Malvern Zeta-sizer 3000.

2.3 Adsorption studies

Acid violet 17 solutions were prepared by dissolving the dye in deionised water. The pH of the water was virtually unchanged on dissolution of the dye and was typically around pH 8. The adsorption kinetic study was conducted by mixing a known mass of adsorbent with 1 L of acid violet 17 solution of known concentration. Mixing was achieved using a magnetic stirrer at 700 rpm. Five millilitre samples were taken at regular intervals analysed for the concentration of acid violet 17 by UV/Vis spectroscopy. Adsorption isotherm data were collected by adding 1 g of adsorbent to 100 mL samples of acid violet 17 solution at a range of concentrations from 10 to 200 mg L⁻¹, and mixing for 60 min to obtain equilibrium. After adsorption, the solution was filtered and analysed for the concentration of acid violet 17.

2.4 Adsorbent bed conductivity

The electrical conductivity of a bed of adsorbent has a significant role in the regeneration process, influencing the regeneration cost and performance. Therefore, the electrical conductivity of the adsorbents was investigated by measuring the drop in voltage across a bed of adsorbent at a range of bed thicknesses and applied currents. The packed beds were prepared in PVC tubes of various lengths

(1–5 cm) with cross-sectional area of 6.0 cm². The electrical resistivity of each adsorbent bed consisting of a mixture of NyexTM 2000 and 1000 with 0.3 % H₂SO₄ electrolyte solution was determined. In order to simulate a bed of adsorbent undergoing electrochemical regeneration, the bed was prepared with a 3 wt% H₂SO₄ electrolyte prepared using deionised water. A 1:1 mass ratio of solution and adsorbent was used for NyexTM 2000 and a 1:4 mass ratio for NyexTM 1000. These ratios were selected to give a saturated bed of adsorbent in each case.

2.5 Electrochemical regeneration

The electrochemical regeneration of NyexTM 2000 and 1000 was investigated in the anodic compartment of a sequential batch electrochemical cell (shown schematically in Fig. 2). The cell was divided into anodic and cathodic compartments by a micro-porous polyethylene membrane (Daramic 350). The cathode was a 1 mm thick perforated plate of 316 stainless steel and the anode current feeder was a graphite plate. Both electrodes had a geometric area of 70 cm² (10 × 35 cm). At the start of each regeneration, the cathode compartment was filled with an aqueous solution of 0.3 wt% NaCl, which was prepared using deionised water and was acidified to pH 2 using hydrochloric acid. This catholyte is similar to that used in previous studies [8, 21, 23] and was required to provide conductivity in the catholyte and for the stability of the Daramic membrane, which requires neutral or acidic conditions. Although chloride is likely to migrate through the membrane and may lead to toxic chlorinated breakdown products, previous studies have shown that these breakdown products are strongly adsorbed on the graphitic adsorbents [23] and are subsequently oxidized to less harmful products [27]. Evaluation of breakdown products is not the focus of this paper; however, this is an important topic that will be considered in detail in future studies.

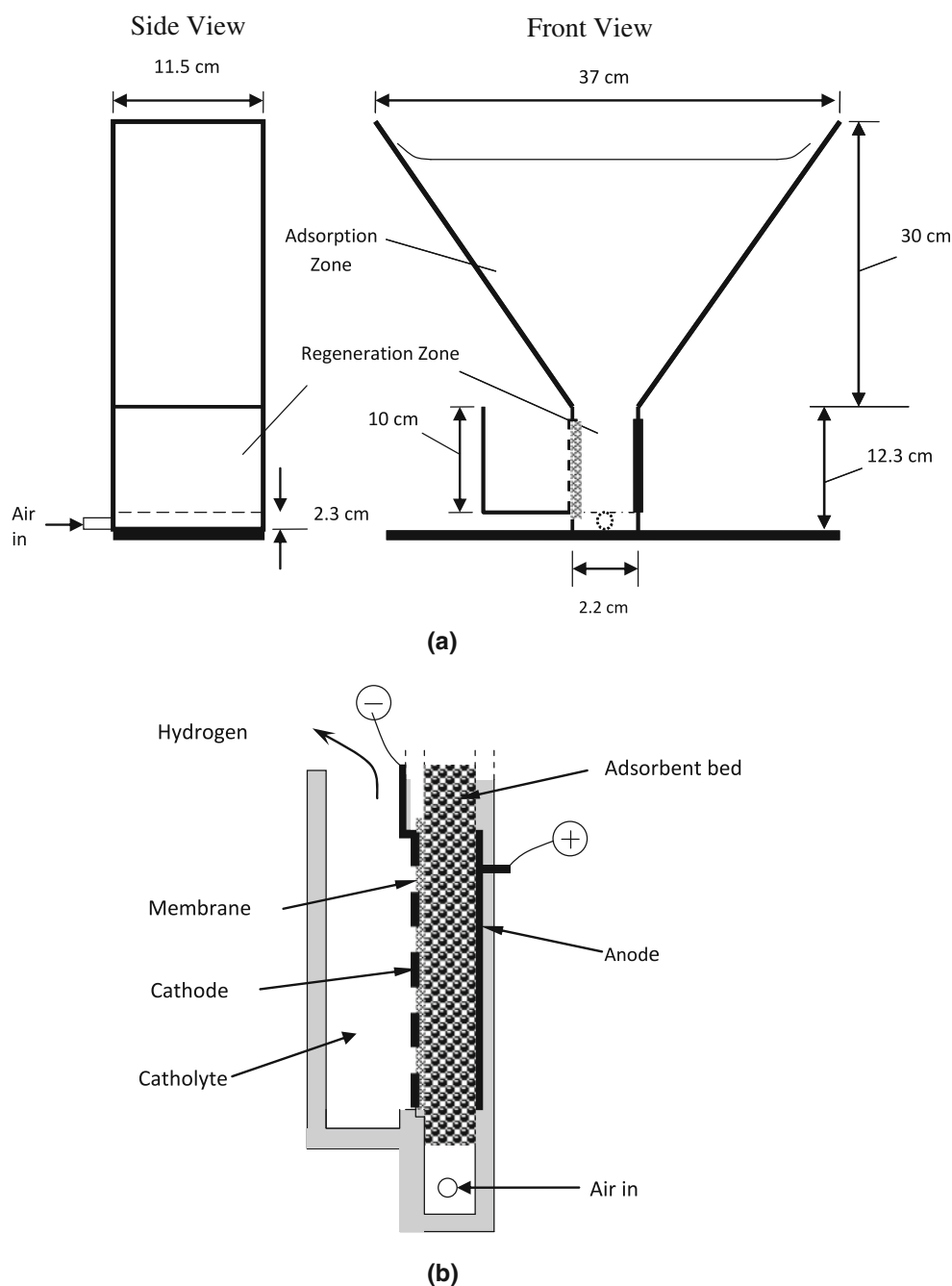
A DC power supply was used to supply a constant current to the electrochemical cell during regeneration. The procedure to determine the regeneration efficiency of Nyex™ 2000 was as follows:

- (i) *Initial adsorption* A known mass of Nyex™ was added to 1 L of deionised water containing a known concentration of acid violet 17 in the sequential batch cell (Fig. 2). The mixture was agitated for 60 min by sparging with air at the base of the cell to obtain equilibrium. After adsorption, the air flow was stopped and the adsorbent was allowed to settle into the anodic

compartment of the electrochemical cell. A sample of the treated liquid was taken and the equilibrium concentration of acid violet 17 after adsorption and thus (by mass balance) the initial adsorbent loading q_i were determined.

- (ii) *Electrochemical regeneration* Once the adsorbent had settled into the electrochemical cell, a DC current was supplied to the cell. There was no flow in the cell and the only mixing was due to the gas bubbles produced in the bed. After regeneration the treated solution was drained off.

Fig. 2 Sequential batch cell for electrochemical regeneration of adsorbent **a** schematic diagram showing *side* and *front* views of the rig, and **b** schematic diagram showing a *cross section* of the electrochemical the regeneration zone



- (iii) *Re-adsorption* Regenerated adsorbent (i.e. the contents of anodic compartment with no further treatment) were mixed by air sparging with a fresh batch of acid violet 17 solution with the same concentration as used in the first adsorption (i). After adsorption the equilibrium concentration of acid violet 17 and thus (by mass balance) the adsorbent loading after regeneration q_r were determined. The loading was always calculated assuming that the loading was zero before adsorption.

From the initial (q_i) and regenerated (q_r) adsorbent loadings, the regeneration efficiency R was defined as:

$$R = \frac{q_r}{q_i} \cdot 100 \%$$

For multiple adsorption/electrochemical regeneration cycles, steps (ii) and (iii) were repeated. To study the effect of bed thickness a small batch electrochemical cell was used (Fig. 3), which was designed to allow the position of the membrane to be varied. In this case, adsorption was carried out in a flask using a magnetic stirrer, and the adsorbent was filtered off from the solution and loaded manually into the anode compartment of the electrochemical cell. No electrolyte was added to the adsorbent bed but as before the cathode compartment was filled with a 0.3 wt% NaCl solution adjusted to pH 2 using HCl.

3 Results and discussion

3.1 Adsorbent characterisation

The physical characteristics of the NyexTM 1000 and NyexTM 2000 adsorbents determined by the methods

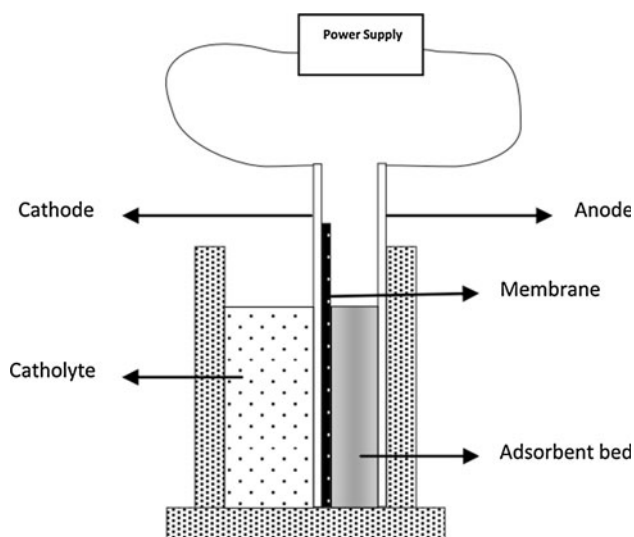


Fig. 3 Schematic diagram of the small batch electrochemical cell with effective anode area of 40 cm² used to study the effect of bed thickness on regeneration efficiency

described in Sect. 2.2 are shown in Table 1. NyexTM 2000 was found to have a BET-specific surface area of 17 m² g⁻¹, much higher than that of NyexTM 1000 which was found to be around 1 m² g⁻¹. The NyexTM 2000 also has a significantly larger average particle size of 784 μm compared to the 484 μm of NyexTM 1000. The nitrogen adsorption analysis indicated that unlike NyexTM 1000, NyexTM 2000 has significant porosity and a much lower bulk density. The porosity of the adsorbent bed was around 0.4 for both adsorbent materials, indicating particle densities of 2.2 g cm⁻³ for NyexTM 1000 (consistent with non-porous graphite) and 0.55 g cm⁻³ for NyexTM 2000. The higher specific surface area of NyexTM 2000 relative to NyexTM 1000 can thus be explained partly by its lower particle density and partly by an increase in surface roughness, evident in Fig. 1. The increase in porosity (Table 1) may also lead to some internal BET surface area in the NyexTM 2000.

The results of Boehm titration revealed that the surface of NyexTM 1000 has significant concentrations of acidic functional groups with no detectable basic functionality (Table 2). The proportion of phenolic groups was found to be dominant at around 78 and 68 % of the total surface functionality of NyexTM 1000 and 2000, respectively. The thermal and mechanical processing of the GIC material was found to have significantly altered the surface chemistry, with NyexTM 2000 having significantly more lactonic groups and around half the amount of phenolic groups when compared to NyexTM 1000. Furthermore, the surface pH (measured using the method described in Sect. 2.2) increased from pH 2 for NyexTM 1000 to pH 5 for NyexTM 2000.

The decrease in oxygen containing surface functional groups during the preparation of NyexTM 2000 is also evident from surface elemental analysis (obtained using energy-dispersive X-ray spectroscopy, EDS, under the electron microscope) as shown in Table 3. Traces of Fe and Si were also detected on the surface as shown in Table 3. However, sulphur was found only on the surface of NyexTM 1000 and was presumably driven off during the thermal treatment for preparation of NyexTM 2000.

Figure 4 shows the variation of the zeta potential of NyexTM 1000 and 2000 with pH. The iso-electric point (IEP) of NyexTM 1000 was found to be approximately pH 5, while the IEP of the NyexTM 2000 was found to be significantly lower (at pH 3) than that of the NyexTM 1000. This is somewhat surprising, as the more acidic surface of the NyexTM 1000 would be expected to have a more negative surface charge than the higher pH NyexTM 2000. The analysis has been repeated several times to confirm the observed behaviour. Further study is needed to explain the zeta potential data, and for the purposes of this study the surface pH (Table 2) is perhaps more

Table 1 Characterisation of NyexTM 1000 and 2000 adsorbents, determined by nitrogen adsorption (BET) and laser diffraction particle size analysis

Adsorbent	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (Å)	Bulk density (g cm ⁻³)	Mean particle diameter (μm)
Nyex TM 1000	1.0	0.0038	134	0.89	484
Nyex TM 2000	17	0.068	163	0.22	754

Table 2 Boehm titration and surface pH of Nyex 1000 and 2000 adsorbents

Adsorbent	Carboxylic groups (mol g ⁻¹)	Lactonic groups (mol g ⁻¹)	Phenolic groups (mol g ⁻¹)	Basic groups (mol g ⁻¹)	Total acidic groups (mol g ⁻¹)	Total surface groups (mol g ⁻¹)	Surface pH
Nyex TM 1000	0.05	0.005	0.195	0	0.25	0.25	2
Nyex TM 2000	0.03	0.014	0.094	0	0.138	0.138	5

Table 3 X-ray (EDS) elemental analysis of Nyex 1000 and 2000 adsorbents

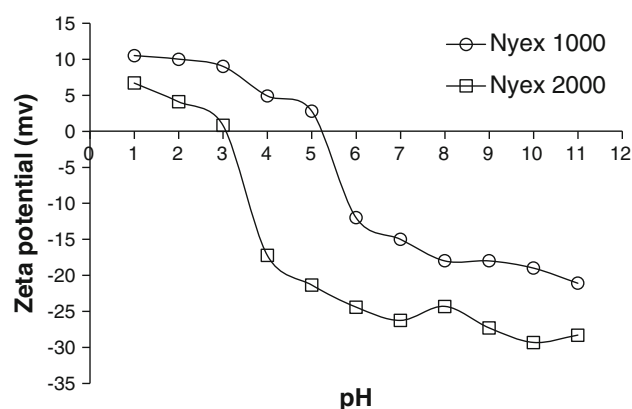
Adsorbent	C wt%	O wt%	S wt%	Fe wt%	Si wt%
Nyex TM 1000	77.88	18.69	3.22	0.17	0.05
Nyex TM 2000	95.77	4.08	Nil	0.13	0.02

representative of the surface characteristics than the isoelectric point.

The electrical conductivity of a bed of NyexTM 2000 was found to be around 1.62 S cm⁻¹, around double that of NyexTM 1000, 0.83 S cm⁻¹. The increased bed conductivity is presumably due to reduced inter-particle contact resistance due to the rougher surface of the NyexTM 2000. The good electrical conductivity of NyexTM 2000 suggests that it will be suitable for electrochemical regeneration and may offer reduced energy consumption.

3.2 Adsorption

The rates of adsorption of acid violet 17 on NyexTM 1000 and NyexTM 2000 were found to be approximately similar. The adsorption was observed to be rapid for each adsorption system (Fig. 5) with more than 75 % of the equilibrium being achieved after 5 min for an initial acid violet 17 concentration of around 100 mg L⁻¹. The nitrogen adsorption data (Table 1) revealed that NyexTM 2000 is partially porous, unlike NyexTM 1000 which is essentially non-porous. However, the porosity was found to have minimal affect on adsorption kinetics suggesting that intra-particle diffusion was rapid or that the adsorption occurred largely on the external surfaces. A mixing time of 60 min was assumed to be sufficient for both adsorbents to attain equilibrium conditions. Some additional adsorption was observed after 60 min with the NyexTM 1000 adsorbent, possibly due to attrition of the adsorbent.

**Fig. 4** Measured values of zeta potential of NyexTM 1000 and 2000 as a function of pH

These results are consistent with those obtained by Brown et al. [8, 21, 22] using a similar range of starting concentrations of crystal violet, atrazine and phenol in which 80–90 % of the equilibrium was reported to be achieved within 2 min using NyexTM 100 adsorbent. NyexTM 100 was reported to be a powdered GIC-bisulphate material. Although, NyexTM 1000 is also a GIC-bisulphate material, it has an average particle size of 484 μm compared to that of 127 μm of NyexTM 100, which probably accounts for the faster adsorption kinetics observed by Brown et al. [22] with the NyexTM 100 adsorbent.

Figure 6 shows the adsorption isotherms obtained for acid violet 17 on NyexTM 1000 and NyexTM 2000 using a mixing time of 60 min. The lines show the Freundlich isotherm ($q_e = kC_e^{1/n}$) fitted to the data using a least squared error method. It is evident from Fig. 6 that NyexTM 2000 delivered an increased maximum adsorptive capacity of 9–10 mg g⁻¹ acid violet 17 compared to that of NyexTM 1000, which was around 3.5 mg g⁻¹. The change in surface area and surface chemistry led to a significant increase

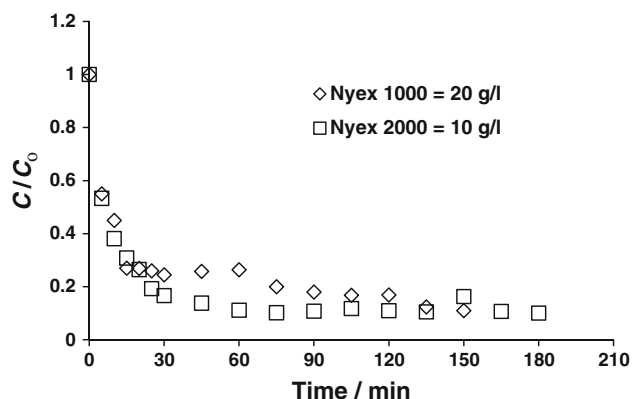


Fig. 5 Adsorption kinetics for adsorption of acid violet 17 on Nyex™ 1000 and Nyex™ 2000 using initial concentrations of 100 and 75 mg L⁻¹, respectively

in the adsorptive capacity for the removal of acid violet 17. However, the increase in adsorptive capacity was not proportional to the increase in specific surface area. In addition, the increase in adsorptive capacity may be associated with the lower level of surface oxides leading to increased charge interactions with the anionic dye.

The adsorption capacities obtained for Nyex™ 1000 are of the same order of magnitude as that reported by Brown et al. [8, 21, 22] for Nyex™ 100 (albeit for different adsorbates: crystal violet, atrazine and phenol), and similar to that reported by Mohammed et al. [25] for acid violet 17 adsorption on Nyex™ 1000.

3.3 Electrochemical regeneration

Electrochemical regeneration was carried out with a range of operating conditions to determine the effect of the key parameters, in particular to the charge passed and the current density. Previous studies have demonstrated the effective electrochemical regeneration of Nyex™ 100 [22] and Nyex™ 1000 [28], and this study will focus on determining the suitable conditions for electrochemical regeneration of Nyex™ 2000.

Figure 7 shows the effect of charge passed per gram of Nyex™ 2000 on its regeneration efficiency. Under the adsorption conditions used, the loading of acid violet on the adsorbent before regeneration was approximately 10 mg g⁻¹. It was found that regeneration efficiency increased with an increase of charge passed. At high values of charge passed, in some cases regeneration efficiencies greater than 100 % were observed, indicating that the regenerated adsorbent had a higher adsorption capacity than the fresh adsorbent. This effect has previously been reported for Nyex™ adsorbents by Brown et al. [8] and has been ascribed to a slight roughening of the adsorbent surface observed after electrochemical treatment.

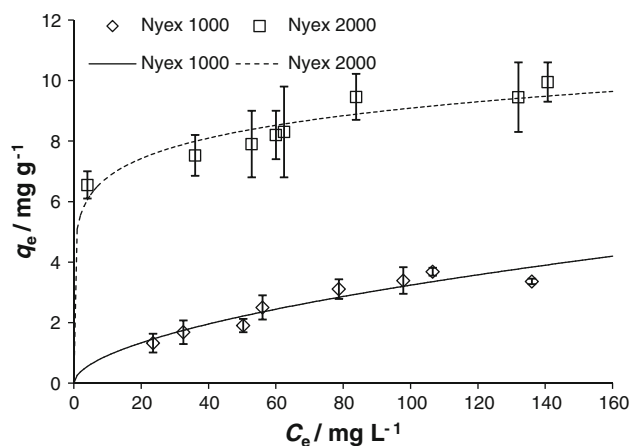


Fig. 6 Adsorption isotherm for adsorption of acid violet 17 on Nyex™ 1000 and Nyex™ 2000 obtained using a contact time of 60 min to achieve equilibrium. Each data point shows the average of two adsorption experiments and the error bars show the range. The lines show the Freundlich isotherms ($q_e = k C_e^{1/n}$) fitted to the data using a least squared error method. The Freundlich coefficients obtained were $k = 0.256 \text{ mg g}^{-1} \text{ L}^{1/n} \text{ mg}^{-1/n}$, $1/n = 0.551$ for Nyex™ 1000 and $k = 5.09 \text{ mg g}^{-1} \text{ L}^{1/n} \text{ mg}^{-1/n}$, $1/n = 0.126$ for Nyex™ 2000

The charge required to achieve 100 % regeneration efficiency was found to be around 80 C g⁻¹ for Nyex™ 2000. This compares with the charge of 36 C g⁻¹ required for 100 % regeneration efficiency of Nyex™ 100 loaded with crystal violet reported by Brown et al. [8] and ~20 C g⁻¹ obtained for Nyex™ 1000 by Mohammed [28]. Thus, the Nyex™ 2000 required significantly more charge for complete regeneration than the Nyex™ 100 and 1000. Although this is consistent with the higher adsorbate loading of Nyex™ 2000, the current efficiency for regeneration of this adsorbent appears to be lower than that of Nyex™ 100. Note that the charge required for regeneration of Nyex™ 2000 is much lower than that reported for granular activated carbon of 1,500 C g⁻¹ for 95 % regeneration [16], even when accounting for the high loading of phenol of 107 mg g⁻¹ on the activated carbon.

Figure 8 shows the effect of current density on the regeneration efficiency of Nyex™ 2000 loaded with acid violet 17. At each current density the regeneration was carried out with the same charge passed (100 C g⁻¹) by varying the duration of the regeneration. A slight decrease in regeneration efficiency was observed with increasing current density. Brown et al. [22] reported a similar trend of decreasing regeneration efficiency with increasing current density for regeneration of Nyex™ 100 loaded with crystal violet. This effect is probably due to increased rates of side reactions, such as oxygen evolution, as the current density was increased. A lower range of current density (10–20 mA cm⁻²) is recommended to minimize the side reactions and ensure efficient regeneration.

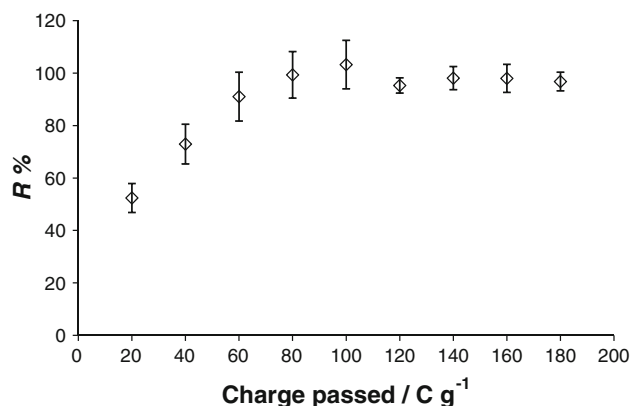


Fig. 7 The effect of charge passed on the regeneration efficiency of the Nyex™ loaded with $\sim 10 \text{ mg g}^{-1}$ of acid violet 17. The adsorbent bed thickness was 2 cm and the current density used was 14 mA cm^{-2}

An increase in cell potential with increased current density was observed resulting in an increase in the power consumption. High current densities may be advantageous due to decreased regeneration time that can reduce the number of cells required for regeneration and thus the capital costs. However, high current densities can reduce the lifetime of the anode due to corrosion and increase the energy consumption due to increased cell potentials and side reactions.

The adsorbent bed thickness determines the number of cells required for electrochemical regeneration for a known mass of adsorbent. Since Nyex™ 2000 was found to have a higher conductivity, experiments were carried out to determine whether a thicker bed of this adsorbent could be regenerated, increasing the current density with bed

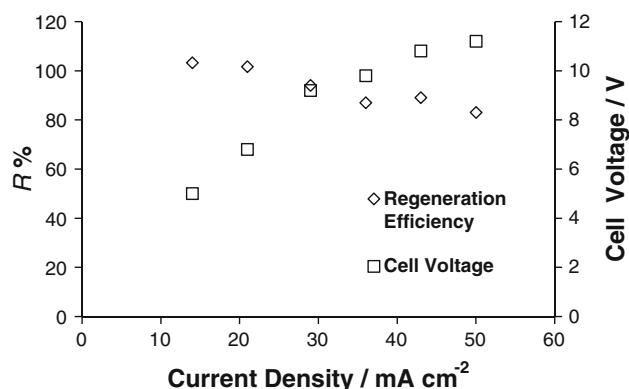


Fig. 8 The effect of current density on regeneration efficiency and cell voltage for electrochemical regeneration of Nyex™ 2000 loaded with $\sim 10 \text{ mg g}^{-1}$ of acid violet 17. The adsorbent bed thickness during regeneration was 2 cm and at each current density a constant charge passed of 100 C g^{-1} was used by varying the duration of the regeneration

thickness to get the same regeneration time for a regeneration charge passed of 100 C g^{-1} . These experiments were performed using the small batch electrochemical cell shown schematically in Fig. 3, which allowed the depth of the anode compartment to be varied.

Figure 9 shows that as the bed thickness increased, high regeneration efficiencies were obtained up to a bed thickness of 30 mm. A bed thickness above 40 mm is not recommended as the regeneration efficiency of Nyex™ 2000 drops significantly and there is an increase in cell potential due to the combined increase in current density and resistance across the adsorbent bed. It is evident from Fig. 9 that Nyex™ 2000 presented high regeneration efficiency ($>90\%$) with increased bed thickness up to a 30 mm bed, which is significantly better, was observed with Nyex™ 100, which gave regeneration efficiency of greater than 80 % for bed thicknesses of up to 20 mm [8]. This increase in the bed thickness which can be used with Nyex™ 2000 effectively reduces the number of cells required to treat the same volume of wastewater by adsorption and electrochemical regeneration process. This will lower the associated capital, operating and maintenance cost of the plant. The improved electrochemical regeneration efficiency observed with a 30 mm bed of Nyex™ 2000 when compared to Nyex™ 100 is presumably due to the high electrical conductivity of the modified adsorbent (see below). However, the relatively low bulk density of the Nyex™ 2000 (Table 1) mitigates against the benefits provided by the improved adsorbent loading and bed thickness.

3.4 Multiple cycles of adsorption and electrochemical regeneration

The performance of Nyex™ 1000 and Nyex™ 2000 was compared by performing multiple cycles of adsorption and regeneration in the sequential batch electrochemical cell shown in Fig. 2. Figures 10 and 11 shows the regeneration efficiency obtained using Nyex™ 1000 and 2000 over five cycles of adsorption and regeneration. In each case, a control experiment was carried out where no current was passed during regeneration. In order to ensure regeneration efficiencies of 100 %, a charge of 36 C g^{-1} was used for Nyex™ 1000 [29] and 80 C g^{-1} for Nyex™ 2000 (see Fig. 7).

When no charge was passed during the regeneration, the regeneration efficiency decreased as the adsorbent became saturated with acid violet 17, as shown in Figs. 10 and 11. The average cell voltage during the electrochemical regeneration was 5 and 4 V for Nyex™ 1000 and Nyex™ 2000 adsorbents, respectively. The lower cell voltage for Nyex™ 2000 is consistent with the higher bed conductivity of this material. If we consider the amount of dye removed from solution and oxidized, the energy

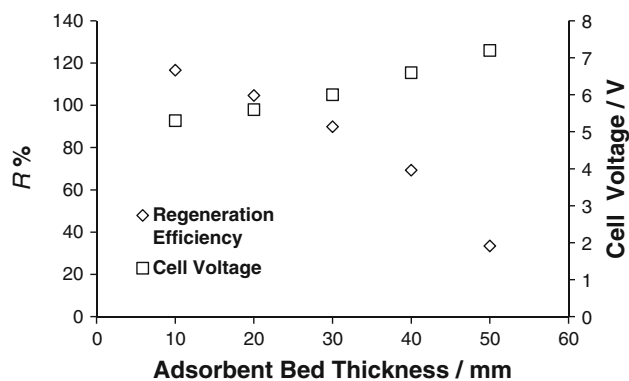


Fig. 9 The effect of adsorbent bed thickness on regeneration efficiency for regeneration of Nyex™ 2000 loaded with $\sim 10 \text{ mg g}^{-1}$ of acid violet 17. The current density was increased (from 12.5 to 50 mA cm^{-2}) in proportion to the bed thicknesses to give a constant regeneration time of 30 min and a charge passed of 100 C g^{-1}

consumption was 51 and 32 J mg^{-1} of dye treated for the Nyex™ 1000 and Nyex™ 2000 adsorbents, respectively. The new adsorbent Nyex™ 2000 thus delivered a three fold increase in adsorptive capacity for acid violet 17 and offered a lower specific electrical energy consumption than the Nyex™ 1000 adsorbent.

The electrochemical regeneration has led to the anodic oxidation of adsorbed acid violet 17 on the surface of the

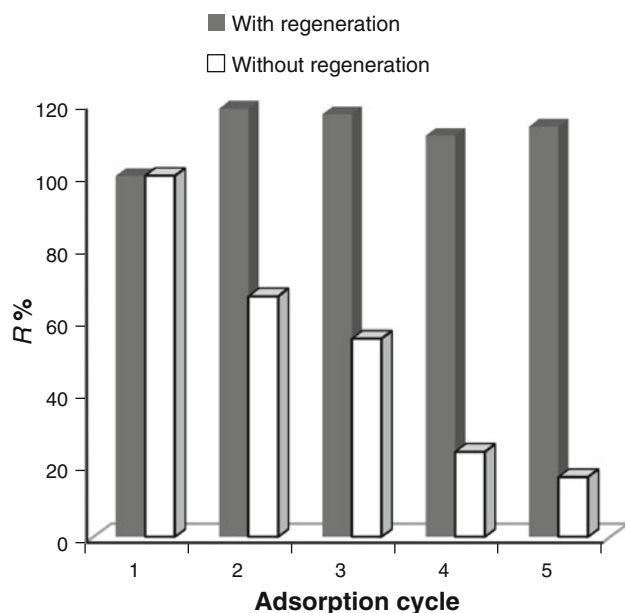


Fig. 10 Regeneration efficiency over five cycles of adsorption and electrochemical regeneration cycles for treatment of acid violet 17 solution using Nyex™ 2000 in the sequential batch cell. Adsorption was carried out using a dose rate of Nyex™ 2000 of 45 g L^{-1} and an initial concentration of acid violet 17 of 500 mg L^{-1} . The regeneration time was 60 min, with a current density of 14 mA cm^{-2} and a charge passed 80 C g^{-1}

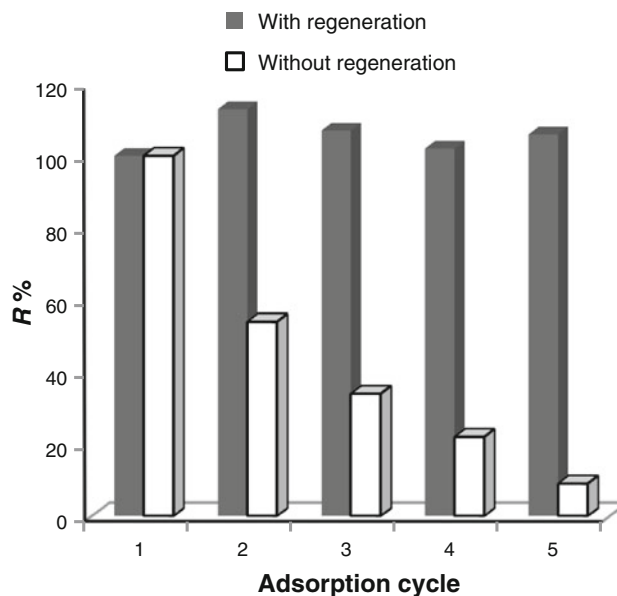


Fig. 11 Regeneration efficiency over five cycles of adsorption and electrochemical regeneration for treatment of acid violet 17 solution using Nyex™ 1000 in the sequential batch cell. Adsorption was carried out using a dose rate of Nyex™ 1000 of 100 g L^{-1} and an initial concentration of acid violet 17 of 800 mg L^{-1} . The regeneration time was 60 min, with a current density of 14 mA cm^{-2} and a charge passed 36 C g^{-1}

adsorbents. After the completion of electrochemical regeneration, the entire contents of the anodic compartment (including any liquid present) were used directly in the next adsorption cycle without further treatment. The products of electrochemical oxidation do not interfere with subsequent adsorption cycles and it is speculated that the contaminant was mineralised to carbon dioxide and water during the electrochemical regeneration process.

3.5 COD analysis

The chemical oxygen demand (COD) is a widely used measure of the organic contamination in industrial effluents. In order to investigate whether any organic breakdown products occur in solution, COD analysis of water after treatment by adsorption and electrochemical was carried out. Figure 12 shows the COD removal achieved after the treatment of 700 and 500 mg L^{-1} acid violet 17 over five adsorption/regeneration cycles using the Nyex 2000 and Nyex 1000 adsorbents, respectively. The treated water was drained off and a fresh batch of contaminated solution was added before each adsorption cycle, and COD analysis was carried out on samples of the initial and treated solutions. A COD removal of above 90 % was achieved through five adsorption/regeneration cycles, while for Nyex 1000 the COD removal was maintained at

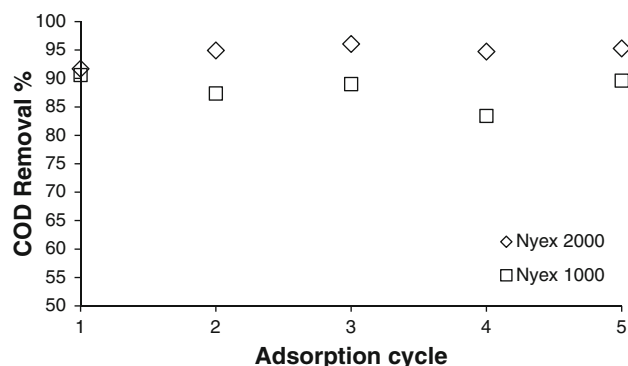


Fig. 12 COD removal obtained during treatment of water contaminated with acid violet 17 using NyexTM 1000 and NyexTM 2000 adsorbent for a series of adsorption/regeneration cycles. Electrochemical regeneration was carried out by passing a current of 1 A for 40 min, with other experimental conditions as used in Fig. 10. The initial acid violet 17 concentration and COD in the water were 780 and 266 mg L⁻¹, respectively, prior to each adsorption cycle. The mass of adsorbent used was 110 g for NyexTM 1000 and 50 g for NyexTM 2000, and the volume of the contaminated water added on each cycle was 1 L

around 85 %. It is not possible to achieve 100 % removal with this treatment process, since it is a batch equilibrium process. However, the observed COD removal is consistent with the removal of acid violet 17 as shown in Fig. 12. The results confirm that the acid violet 17 contaminant was treated effectively and very little organic contamination was observed in the treated water.

4 Conclusions

The new adsorbent material NyexTM 2000 was found to have an adsorptive capacity of around two to three times higher than that of the previously used NyexTM 1000. The ratio of the adsorptive capacities of these two materials is much less than the ratio of specific surface areas. Analysis of the surface charge and functional groups present showed that there were significant differences, suggesting that the processing used to prepare the NyexTM 2000 has modified the surface chemistry. Further study is needed to investigate whether surface treatment can be used to improve the adsorptive capacity of the new adsorbent.

In addition to improved adsorption capacity, the electrical conductivity of a bed of NyexTM 2000 was around double that of NyexTM 1000. The new adsorbent was found to be suitable for electrochemical regeneration with ~100 % regeneration achieved using a charge passed of 80 C g⁻¹, which is higher than that required for NyexTM 1000, reflecting the higher adsorptive capacity. The higher conductivity of the NyexTM 2000 bed enables electrochemical regeneration with reduced electrical energy

consumption or the use of a thicker adsorbent bed. However, some of the benefits of the new NyexTM 2000 adsorbent are mitigated by its low bulk density (around 25 % of that of NyexTM 1000), so that a larger amount of electrode area will be required to regenerate the same mass of adsorbent. In spite of this, the specific electrical energy consumption for treatment of acid violet 17 by adsorption and electrochemical regeneration was around 36 % lower with NyexTM 2000 when compared to NyexTM 1000. The findings of this study have shown that for some applications, this new adsorbent material may offer significant advantages over the existing adsorbent material. Further study is needed to investigate the surface chemistry of this new adsorbent. Efforts should be directed towards the development of GIC-based adsorbent materials which offer increased capacity while maintaining a high bulk density.

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